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Registry No. $\{\text{Fe}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2\}_2$, 19570-24-2; $[\text{Fe}(\mu_3\text{-CO})(\eta^5\text{-C}_5\text{H}_5)_4]$, 12203-87-1; $\text{S}_2\text{C}_2(\text{CF}_3)_2$, 55162-21-5; $\text{Fe}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2\text{CO}$, 55162-25-9; $\eta^5\text{-C}_5\text{H}_5\text{Fe}[\text{S}_2\text{C}_2(\text{CF}_3)_2]$, 12261-16-4.

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- (6) (a) No reaction is effected upon bubbling carbon monoxide through a dichloromethane solution of $(\text{Bu}_4\text{N})_2\text{Fe}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$. (b) This equilibrium is further suggested by the decomposition of $\text{Fe}(\text{CO})[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2$ to the starting material with dry nitrogen gas in dichloromethane.
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Resonance Raman Spectra of Metal Complexes of Substituted Dithiophosphinic Acids^{1a}

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Resonance Raman scattering may occur if the exciting radiation falls within an electronic absorption band of the scattering molecule.² The intensity of the Raman lines arising from vibrations coupled to the electronic transition may be increased by several orders of magnitude compared with their intensity in normal Raman spectra thus enabling Raman spectroscopic investigations to be carried out at very low concentrations of the chromophoric scattering moiety. In this communication we report the resonance Raman scattering observed from three metal complexes of dithiophosphinic acid derivatives $\text{Ni}[\text{S}_2\text{P}(\text{OEt})_2]_2$, $\text{Ni}[\text{S}_2\text{PPh}_2]_2$, and $\text{Cr}[\text{S}_2\text{PPh}_2]_3$. The physical properties of these compounds have been studied earlier but their Raman spectra were not obtained as these compounds show strong self-absorption.^{3,4}

Many papers have appeared recently dealing with the resonance Raman spectra of biological systems containing MS_n chromophores (see ref 5 and references cited therein). The spectral information obtained about the complexes described in this paper (having well-defined geometries) may be of interest in the resonance Raman studies of such biological systems.

Experimental Section

Pure crystalline samples of $\text{Ni}[\text{S}_2\text{PPh}_2]_2$, $\text{Ni}[\text{S}_2\text{P}(\text{OEt})_2]_2$, and $\text{Cr}[\text{S}_2\text{PPh}_2]_3$ were kindly supplied by Dr. R. G. Cavell of the University of Alberta, Edmonton, Alberta, Canada.^{3,4} Raman spectra of the dilute ($\sim 5 \times 10^{-3} M$) solutions in CS_2 and CH_2Cl_2 were recorded using a rotating cell to avoid local heating.⁶ In addition, spectra of $\text{Ni}[\text{S}_2\text{PPh}_2]_2$ and $\text{Cr}[\text{S}_2\text{PPh}_2]_3$ were recorded as solids dispersed in KBr pellets and again the rotating-cell technique was used.^{7,8} All spectra were recorded at a resolution of $\sim 5 \text{ cm}^{-1}$ and the other details of the spectroscopic method used here have been described earlier.⁹

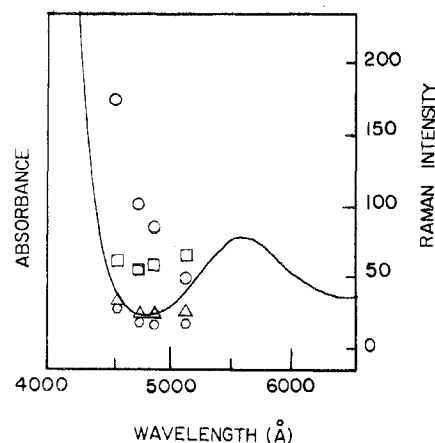


Figure 1. Absorption spectrum of $\sim 0.005 M \text{Cr}[\text{S}_2\text{PPh}_2]_3$ in CS_2 solution. Relative Raman intensities of the above solution as a function of the exciting wavelength for the bands at 282 (\circ), 999 (\square), 1029 (\triangle), and 1101 cm^{-1} (∇).

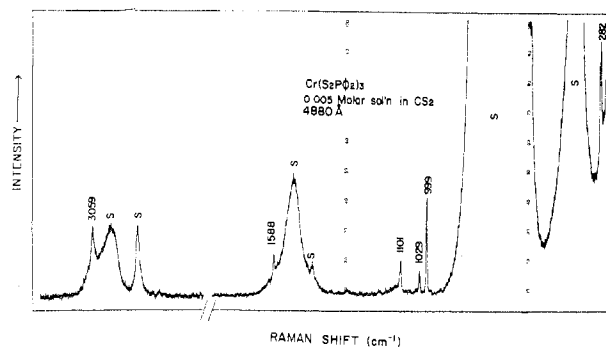


Figure 2. Resonance Raman spectrum of $\text{Cr}[\text{S}_2\text{PPh}_2]_3$ in CS_2 solution; spectral slit width $\sim 5 \text{ cm}^{-1}$; laser power $\sim 1 \text{ W}$. S denotes solvent (CS_2) bands.

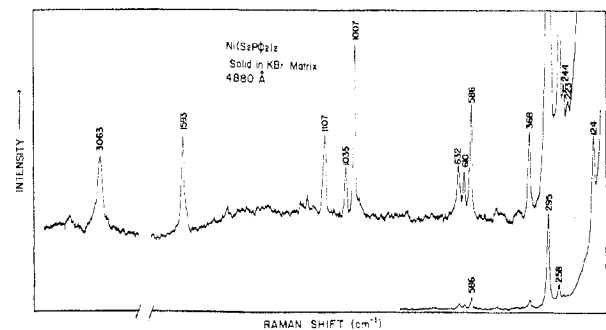


Figure 3. Resonance Raman spectrum of solid $\text{Ni}[\text{S}_2\text{PPh}_2]_2$ dispersed in KBr matrix; spectral slit width $\sim 5 \text{ cm}^{-1}$; laser power at the sample $\sim 400 \text{ mW}$.

Results and Discussion

The absorption spectrum of $\sim 0.005 M \text{Cr}[\text{S}_2\text{PPh}_2]_3$ in CS_2 solution is shown in Figure 1 for the 4000–6500-Å region. The CS_2 solution spectra of the three complexes agreed closely with those reported earlier in CH_2Cl_2 solutions, indicating thereby that the complexes are monomeric and stable in CS_2 .^{3,4} The Raman spectra of $\text{Cr}[\text{S}_2\text{PPh}_2]_3$ in CS_2 solution and of $\text{Ni}[\text{S}_2\text{PPh}_2]_2$ as solid dispersed in KBr matrix are shown in Figures 2 and 3, respectively. The frequencies of the observed features in the Raman spectra of $\text{Ni}[\text{S}_2\text{PPh}_2]_2$ and $\text{Cr}[\text{S}_2\text{PPh}_2]_3$, both as solids and as solutions in CS_2 and CH_2Cl_2 are given in Table I. The frequency accuracy is $\pm 2 \text{ cm}^{-1}$. Table I also contains the depolarization ratios of the observed features in the solution spectra as obtained with 4880-Å excitations. Three additional lines of Ar^+ laser, 4579, 4765, and 5145 Å, were also used to record the Raman spectra. The

Table I. Raman Spectra of Metal Complexes of Diphenyldithiophosphinic Acid

Ni[S ₂ PPh ₂] ₂					Cr[S ₂ PPh ₂] ₃					Assignment
Solid		CS ₂ soln			Solid		CS ₂ soln			
$\Delta\nu$, cm ⁻¹	Intens ^a	$\Delta\nu$, cm ⁻¹	Intens ^a	ρ_1^b	$\Delta\nu$, cm ⁻¹	Intens ^a	$\Delta\nu$, cm ⁻¹	Intens ^a	ρ_1^b	
124	ms									
223	w				227 ± 4	w				
244	w				247 ± 4	sh				
258	ms									
295	s	286	s	0.27	290	s	282	vs	p	Sym ν_{M-S}
368	m	366 ^c	vw	p	365	m				$\nu_{P-S}^{?d}$
586	m	585 ^c	w	p	580	m				
610	w									
632	w									
1007	ms	1001	m	0.06	1007	ms	999	s	0.06	} ν_{C-C} and δ_{HCC}
1035	w	1030	w	0.01	1035	vw	1029	mw		
1107	m	1103	mw	0.05	1109	m	1101	m	0.16	
1593	m	1591	vw	dp?	1593	m	1588	w	dp?	
3063	m	3060	mw	p	3063	m	3059	m	p	ν_{C-H}

^a s, m, w, v, and sh stand for strong, medium, weak, very, and shoulder, respectively. Intensities for 4880-Å excitation. ^b Depolarization ratios where quoted are accurate to ±10% and are for 4880-Å excitation. All strong and medium-intensity bands showed similar depolarization ratios with the other three excitation lines used in this work. ^c CH₂Cl₂ solution. ^d Infrared data; see ref 3 and 4.

intensity of the four bands at 282, 999, 1029, and 1101 cm⁻¹ in the Raman spectra of Cr[S₂PPh₂]₃ solution are plotted as a function of excitation frequency in Figure 1. These intensities were obtained using the 800-cm⁻¹ doublet of CS₂ as the internal standard and were corrected for the instrumental response.⁹

The intensity of the polarized band at 282 cm⁻¹ in the solution spectra of Cr[S₂PPh₂]₃ shows strong resonance enhancement as the exciting line frequency moves toward the high-frequency region. Its intensity at 4579 Å is about four times greater than that observed with 5145-Å excitation, Figure 1. The intensity of this Raman band is mainly enhanced by the uv absorption band(s) and not by the visible absorption band (centered at about 5700 Å) as the Raman band has greater intensity with 4880-Å excitation than with 5145-Å excitation although the latter wavelength occurs in the region of greater absorption of 5700-Å band, Figure 1. Cavell et al.^{3,4} have suggested that the absorption in the visible region is caused by d-d transitions of Cr(III) and that the uv absorption bands are charge transfer and intraligand in origin. The Raman band at 282 cm⁻¹ is assigned to symmetric Cr-S stretching vibration, Table I, as such a vibration is expected to be resonance enhanced by the charge-transfer absorption. The bands at 1029 and 1101 cm⁻¹ show very small intensity enhancement with the decrease in the wavelength of the exciting radiation. These two bands and the one at 999 cm⁻¹ most probably arise from the vibrations of the phenyl groups and hence are expected to show resonance enhancement only when the excitation frequency is in or close to the intraligand bands which are expected to occur at much higher frequencies than the ones used here.¹⁰ The horizontally aligned bands in Table I show similar dependence of their intensities on the excitation frequency for both compounds. The bands above 900 cm⁻¹ are very similar in nature and it seems reasonable to associate them with the phenyl rings in both complexes.

Raman spectra of Ni[S₂P(OEt)₂]₂ in CS₂ solution showed only one strong polarized band at 309 cm⁻¹ having $\rho_1 = 0.2 \pm 0.03$ with 4880-Å excitation. No feature was observed above the 900-cm⁻¹ region under the conditions similar to those used for Ni[S₂PPh₂]₂ and Cr[S₂PPh₂]₃. This again supports the assignment of the features above 900 cm⁻¹ in phenyl derivatives to the vibrations of the phenyl groups, Table I. The band at 309 cm⁻¹ in Ni[S₂P(OEt)₂]₂ is strong and polarized and has an excitation profile (intensity vs. excitation frequency plot) very similar to that seen for the 286-cm⁻¹ band in the solution spectrum of Ni[S₂PPh₂]₂. Therefore it is believed that it also arises mainly from the symmetric Ni-S stretching vibrations. Thus the symmetric Ni-S stretch increases by ~23 cm⁻¹ in

Ni[S₂PX₂]₂ complexes where X = Ph is replaced by X = OEt. This is in agreement with the results obtained from the infrared spectra of these complexes.⁴ The increase in frequency on replacement of phenyl groups by ethoxy groups is consistent with the fact that the Ni-S bond is slightly shorter in ethoxy compounds than in compounds with phenyl groups.⁴

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Registry No. Ni[S₂P(OEt)₂]₂, 16743-23-0; Ni[S₂PPh₂]₂, 22239-85-6; Cr[S₂PPh₂]₃, 14871-17-1.

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Stepwise Formation of Macrocyclic Ligands Containing Nitrogen Donors

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The importance of metal complexes containing synthetic macrocyclic ligands as models for a variety of biochemical processes is now well recognized. However, although there

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